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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C11D 17/00, 3/386, 3/33, 3/39

A1

(11) International Publication Number: WO 99/00478

(43) International Publication Date: 7 January 1999 (07.01.99)

(21) International Application Number: PCT/US98/13187

(22) International Filing Date: 25 June 1998 (25.06.98)

(30) Priority Data:
60/051,162 27 June 1997 (27.06.97) US

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(81) Designated States: BR, CA, CN, JP, MX, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: NON-AQUEOUS LIQUID DETERGENT COMPOSITIONS CONTAINING ENZYME PARTICLES

(57) Abstract

A non-aqueous liquid detergent composition comprising a bleaching agent and/or bleach precursor, one or more of an enzyme particle, characterized in that said detergent composition further comprises ethylenediamine-N, N'-disuccinic acid, or alkali metal, alkaline earth, ammonium or substituted ammonium salts thereof, or mixtures thereof.

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NON-AQUEOUS LIQUID DETERGENT COMPOSITIONS CONTAINING ENZYME PARTICLES

FIELD OF THE INVENTION

This invention relates to liquid laundry detergent products which are non-aqueous in nature and which contain stabilized enzyme particles.

BACKGROUND OF THE INVENTION

Detergent products in the form of liquid are often considered to be more convenient to use than are dry powdered or particulate detergent products. Said detergents have therefore found substantial favour with consumers. Such detergent products are readily measurable, speedily dissolved in the wash water, capable of being easily applied in concentrated solutions or dispersions to soiled areas on garments to be laundered and are non-dusting. They also usually occupy less storage space than granular products. Additionally, such detergents may have incorporated in their formulations materials which could not withstand drying operations without deterioration, which operations are often employed in the manufacture of particulate or granular detergent products.

Although said detergents have a number of advantages over granular detergent products, they also inherently possess several disadvantages. In particular, detergent composition components which may be compatible with each other in granular products may tend to interact or react with each other. Thus such components as enzymes, surfactants, perfumes, brighteners, solvents and especially bleaches and bleach activators can be especially difficult to incorporate into liquid detergent products which have an acceptable degree of chemical stability.

One approach for enhancing the chemical compatibility of detergent composition components in detergent products has been to formulate non-aqueous (or anhydrous) detergent compositions. In such non-aqueous

products, at least some of the normally solid detergent composition components tend to remain insoluble in the liquid product and hence are less reactive with each other than if they had been dissolved in the liquid matrix. Non-aqueous liquid detergent compositions, including those which contain reactive materials such as peroxygen bleaching agents, have been disclosed for example, in Hepworth et al., U.S. Patent 4,615,820, Issued October 17, 1986; Schultz et al., U.S. Patent 4,929,380, Issued May 29, 1990; Schultz et al., U.S. Patent 5,008,031, Issued April 16, 1991; Elder et al., EP-A-030,096, Published June 10, 1981; Hall et al., WO 92/09678, Published June 11, 1992 and Sanderson et al., EP-A-565,017, Published October 13, 1993.

A particular problem that has been observed with the incorporation of enzymes in non-aqueous detergents, containing bleaching agent and/or bleach precursors includes the chemical stability of the enzymes upon dilution in the wash liquor.

Given the foregoing, there is clearly a continuing need to identify and provide said detergent compositions in the form of liquid products that have an efficient enzymatic detergency performance in the wash liquor.

Accordingly, it is an object of the present invention to provide said detergent composition wherein the enzymes are still effective in the wash liquor.

SUMMARY OF THE INVENTION

According to the present invention, there is provided a liquid non-aqueous detergent composition containing bleaching agent and/or bleach precursor which is in the form of a liquid, containing an enzyme characterized in that said compositions further comprise ethylenediamine-N-N'disuccinic acid.

DETAILED DESCRIPTION OF THE INVENTION

Enzyme particles

The enzyme particles suitable for the present invention comprise one or more enzymes which provide cleaning performance and/or fabric care benefits.

Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, ß-glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

A preferred combination is a cleaning composition having cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, which discloses fungal cellulase produced from Humicola insolens. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800.

Other suitable cellulases are cellulases originated from Humicola insolens having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17243.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, laccase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996.

Preferred enhancers are substitued phenthiazine and phenoxasine 10-Phenothiazinepropionicacid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substitued syringates (C3-C5 substitued alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said cellulases and/or peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by micro-organisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable

lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R(Novo) which have found to be very effective when used in combination with the compositions of the present invention.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).
The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. Other preferred proteases include those of WO 95/10591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo.

In more detail, protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said

carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994. Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO91/06637.

Preferred protease for use in the present invention are SAVINASE® and the proteases described in EP 215 446 and WO95/10591 at a level of from 0.001% to 0.5%, preferably from 0.003% to 0.2%, more preferably from 0.01% to 0.1% pure enzyme by weight of total composition for liquid detergent compositions and; SAVINASE®, ALCALASE® and the proteases described in WO91/06637 and WO95/10591 at a level of from 0.0001% to 0.2%, preferably from 0.001% to 0.1%, more preferably 0.005% to 0.05% pure enzyme by weight of total composition in granular detergent compositions.

Highly preferred enzymes to be included are amylases. Amylases (α and/or ß) can be included for removal of carbohydrate-based stains. WO/94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO/94/18314, Genencor, published August 18, 1994 and WO/95/10603, Novo Nordisk A/S, published April 20,1995. Other amylases known for use in cleaning compositions include both α- and β-amylases. α-Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylase are stability-enhanced amylases including Purafact Ox Am^R described in WO 94/18314, published August 18, 1994 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95.

Examples of commercial α-amylases products are Termamyl®, Ban® , Fungamyl® and Duramyl®, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α-amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α-amylase activity assay. Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulatescontaining one enzyme) or as mixtures of two or more enzymes (e.g. cogranulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in co-pending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful Bacillus, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Preferred enzyme particles according to the present invention are characterized by having a reduced average particle size less than 600 microns, preferably between 50 and 500 microns, most preferred between 100 and 400 microns. Stated particle sizes are the diameters of particles of equal volume. Desirably, the particle size distribution is relatively narrow so that average particle sizes expressed as number average or weight average sizes are similar. Particle sizes can be measured, for example, using Coulter counters or laser particle size measuring equipment such as that sold under the Malvern name.

The enzyme particles are prepared by grinding in a mill which will break down the particles to diameters below 600 microns. The enzyme particles will generally be supplied as much larger particles of above about 600 microns diameter. If desired, the enzyme particle may be premixed with other solids (e.g. builders, enzymes). Preferred mills are colloid mills.

Preferred enzyme particles have reduced particle size, since said particles are physically and chemically stable in the concentrate, while at the same time being more effective in the wash liquor.

The compositions of the invention contain, as an essential component, from about 0.01% to about 10%, preferably from about 0.05% to about 2%, of ethylenediamine-N, N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds for liquid detergent compositions are the free acid form and sodium or potassium salts thereof. EDDS are described in US patent 4,704,233.

According to the present invention, it has been found that EDDS effectively improves the efficiency of enzymes, especially amylases, in liquid non-aqueous detergent compositions upon dilution in the wash liquor.

Without being bound by theory, it is believed that ethylenediamine-N, N'-disuccinic acid or its salts act to bind heavy metal ions thereby preventing that heavy metal ions bind at the active site of the enzyme. The binding of

heavy metal ions at the active site of the enzyme results in generation of OH free radicals within the enzyme, resulting in destruction of the enzyme.

Chelating Agents - The liquid non-aqueous detergent compositions according to the present invention may also contain other chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetraproprionates, triethylenetetra-aminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at lease low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

These chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, the chelating agents will comprise from about 0.1% to about 3.0% by weight of the non-aqueous liquid detergent composition.

The non-aqueous detergent compositions of this invention may further comprise a surfactant- and low-polarity solvent-containing liquid gel phase having dispersed therein the enzyme particles. The components of the liquid and solid phases of the detergent compositions herein, as well as composition form, preparation and use, are described in greater detail as follows:

All concentrations and ratios are on a weight basis unless otherwise specified.

Surfactant

The amount of the surfactant mixture component of the detergent compositions herein can vary depending upon the nature and amount of other composition components and depending upon the desired rheological properties of the ultimately formed composition. Generally, this surfactant mixture will be used in an amount comprising from about 10% to 90% by weight of the composition. More preferably, the surfactant mixture will comprise from about 15% to 50% by weight of the composition.

A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in US Patent 3,664,961 issued to Norris on May 23, 1972.

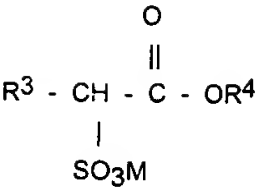
Highly anionic preferred surfactants are the linear alkyl benzene sulfonate (LAS) materials. Such surfactants and their preparation are described for example in U.S. Patents 2,220,099 and 2,477,383, incorporated herein by reference. Especially preferred are the sodium and potassium linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 14. Sodium C_{11}-C_{14}, e.g., C_{12}, LAS is especially preferred.

Other suitable surfactants include the alkyl sulfate surfactants hereof are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10}-C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10}-C_{18} alkyl component, more preferably a C_{12}-C_{15} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations).

Highly preferred anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO3M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, more preferably C_{12}-C_{15} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations Exemplary surfactants are C_{12}-C_{15} alkyl polyethoxylate (1.0) sulfate (C_{12}-$C_{15}E(1.0)M$), C_{12}-C_{15} alkyl polyethoxylate (2.25) sulfate (C_{12}-$C_{15}E(2.25)M$), C_{12}-C_{15} alkyl polyethoxylate (3.0) sulfate (C_{12}-$C_{15}E(3.0)M$), and C_{12}-C_{15} alkyl polyethoxylate (4.0) sulfate (C_{12}-$C_{15}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

Other suitable anionic surfactants to be used are alkyl ester sulfonate surfactants including linear esters of C_8-C_{20} carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula:



wherein R^3 is a C_8-C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1-C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations. Preferably, R^3 is C_{10}-C_{16} alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is C_{10}-C_{16} alkyl.

Other anionic surfactants useful for detersive purposes can also be included in the laundry detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9-C_{20} linear alkylbenzenesulfonates, C_8-C_{22} primary of secondary alkanesulfonates, C_8-C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8-C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C_{12}-C_{18} monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C_6-C_{12} diesters), sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), and alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_k$-CH_2COO-M+ wherein R is a C_8-C_{22} alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and

hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

When included therein, the detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 5% to about 25% by weight of such anionic surfactants.

One class of nonionic surfactants useful in the present invention are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 14, more preferably from 12 to 14. The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Especially preferred nonionic surfactants of this type are the C_9-C_{15} primary alcohol ethoxylates containing 3-12 moles of ethylene oxide per mole of alcohol, particularly the C_{12}-C_{15} primary alcohols containing 5-8 moles of ethylene oxide per mole of alcohol.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula

$$RO\,(C_nH_{2n}O)_tZ_x$$

wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent are disclosed in EP-B 0 070 077, 0 075 996 and

0 094 118.

Also suitable as nonionic surfactants are poly hydroxy fatty acid amide surfactants of the formula

$$R^2 - C - N - Z,$$
$$\| \quad |$$
$$O \quad R^1$$

wherein R^1 is H, or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R^1 is methyl, R^2 is a straight C_{11-15} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

Non-aqueous Liquid Diluent

To form the liquid phase of the detergent compositions, the hereinbefore described surfactant (mixture) may be combined with a non-aqueous liquid diluent such as a liquid alcohol alkoxylate material or a non-aqueous, low-polarity organic solvent.

Alcohol Alkoxylates

One component of the liquid diluent suitable to form the compositions herein comprises an alkoxylated fatty alcohol material. Such materials are themselves also nonionic surfactants. Such materials correspond to the general formula:

$$R^1(C_mH_{2m}O)_nOH$$

wherein R^1 is a C_8 - C_{16} alkyl group, m is from 2 to 4, and n ranges from about 2 to 12. Preferably R^1 is an alkyl group, which may be primary or secondary, that contains from about 9 to 15 carbon atoms, more preferably from about 10 to 14 carbon atoms. Preferably also the alkoxylated fatty alcohols will be ethoxylated materials that contain from about 2 to 12

ethylene oxide moieties per molecule, more preferably from about 3 to 10 ethylene oxide moieties per molecule.

The alkoxylated fatty alcohol component of the liquid diluent will frequently have a hydrophilic-lipophilic balance (HLB) which ranges from about 3 to 17. More preferably, the HLB of this material will range from about 6 to 15, most preferably from about 8 to 15.

Examples of fatty alcohol alkoxylates useful as one of the essential components of the non-aqueous liquid diluent in the compositions herein will include those which are made from alcohols of 12 to 15 carbon atoms and which contain about 7 moles of ethylene oxide. Such materials have been commercially marketed under the trade names Neodol 25-7 and Neodol 23-6.5 by Shell Chemical Company. Other useful Neodols include Neodol 1-5, an ethoxylated fatty alcohol averaging 11 carbon atoms in its alkyl chain with about 5 moles of ethylene oxide; Neodol 23-9, an ethoxylated primary C_{12} - C_{13} alcohol having about 9 moles of ethylene oxide and Neodol 91-10, an ethoxylated C_9 - C_{11} primary alcohol having about 10 moles of ethylene oxide. Alcohol ethoxylates of this type have also been marketed by Shell Chemical Company under the Dobanol tradename. Dobanol 91-5 is an ethoxylated C_9-C_{11} fatty alcohol with an average of 5 moles ethylene oxide and Dobanol 25-7 is an ethoxylated C_{12}-C_{15} fatty alcohol with an average of 7 moles of ethylene oxide per mole of fatty alcohol.

Other examples of suitable ethoxylated alcohols include Tergitol 15-S-7 and Tergitol 15-S-9 both of which are linear secondary alcohol ethoxylates that have been commercially marketed by Union Carbide Corporation. The former is a mixed ethoxylation product of C_{11} to C_{15} linear secondary alkanol with 7 moles of ethylene oxide and the latter is a similar product but with 9 moles of ethylene oxide being reacted.

Other types of alcohol ethoxylates useful in the present compositions are higher molecular weight nonionics, such as Neodol 45-11, which are similar ethylene oxide condensation products of higher fatty alcohols, with the higher fatty alcohol being of 14-15 carbon atoms and the number of ethylene oxide groups per mole being about 11. Such products have also been commercially marketed by Shell Chemical Company.

The alcohol alkoxylate component when utilized as part of the liquid diluent in the non-aqueous compositions herein will generally be present to the extent of from about 1% to 60% by weight of the composition. More preferably, the alcohol alkoxylate component will comprise about 5% to 40% by weight of the compositions herein. Most preferably, the alcohol alkoxylate component will comprise from about 10% to 25% by weight of the detergent compositions herein.

Non-aqueous Low-Polarity Organic Solvent

Another component of the liquid diluent which may form part of the detergent compositions herein comprises non-aqueous, low-polarity organic solvent(s). The term "solvent" is used herein to connote the non-surface active carrier or diluent portion of the liquid phase of the composition. While some of the essential and/or optional components of the compositions herein may actually dissolve in the "solvent"-containing phase, other components will be present as particulate material dispersed within the "solvent"-containing phase. Thus the term "solvent" is not meant to require that the solvent material be capable of actually dissolving all of the detergent composition components added thereto.

The non-aqueous organic materials which are employed as solvents herein are those which are liquids of low polarity. For purposes of this invention, "low-polarity" liquids are those which have little, if any, tendency to dissolve one of the preferred types of particulate material used in the compositions herein, i.e., the peroxygen bleaching agents, sodium perborate or sodium percarbonate. Thus relatively polar solvents such as ethanol should not be utilized. Suitable types of low-polarity solvents useful in the non-aqueous liquid detergent compositions herein do include alkylene glycol mono lower alkyl ethers, lower molecular weight polyethylene glycols, lower molecular weight methyl esters and amides, and the like.

A preferred type of non-aqueous, low-polarity solvent for use herein comprises the mono-, di-, tri-, or tetra- C_2-C_3 alkylene glycol mono C_2-C_6 alkyl ethers. The specific examples of such compounds include diethylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, dipropolyene

glycol monoethyl ether, and dipropylene glycol monobutyl ether. Diethylene glycol monobutyl ether and dipropylene glycol monobutyl ether are especially preferred. Compounds of the type have been commercially marketed under the tradenames Dowanol, Carbitol, and Cellosolve.

Another preferred type of non-aqueous, low-polarity organic solvent useful herein comprises the lower molecular weight polyethylene glycols (PEGs). Such materials are those having molecular weights of at least about 150. PEGs of molecular weight ranging from about 200 to 600 are most preferred.

Yet another preferred type of non-polar, non-aqueous solvent comprises lower molecular weight methyl esters. Such materials are those of the general formula: R^1-C(O)-OCH_3 wherein R^1 ranges from 1 to about 18. Examples of suitable lower molecular weight methyl esters include methyl acetate, methyl propionate, methyl octanoate, and methyl dodecanoate.

The non-aqueous, low-polarity organic solvent(s) employed should, of course, be compatible and non-reactive with other composition components, e.g., bleach and/or activators, used in the liquid detergent compositions herein. Such a solvent component will generally be utilized in an amount of from about 1% to 60% by weight of the composition. More preferably, the non-aqueous, low-polarity organic solvent will comprise from about 5% to 40% by weight of the composition, most preferably from about 10% to 25% by weight of the composition.

Liquid Diluent Concentration

As with the concentration of the surfactant mixture, the amount of total liquid diluent in the compositions herein will be determined by the type and amounts of other composition components and by the desired composition properties. Generally, the liquid diluent will comprise from about 20% to 95% by weight of the compositions herein. More preferably, the liquid diluent will comprise from about 50% to 70% by weight of the composition.

SOLID PHASE

The non-aqueous detergent compositions herein may further comprise a solid phase of particulate material which is dispersed and suspended within the liquid phase. Generally such particulate material will range in size from about 0.1 to 1500 microns. More preferably such material will range in size from about 5 to 500 microns.

The particulate material utilized herein can comprise one or more types of detergent composition components which in particulate form are substantially insoluble in the non-aqueous liquid phase of the composition. The types of particulate materials which can be utilized are described in detail as follows:

Peroxygen Bleaching Agent With Optional Bleach Activators

The most preferred type of particulate material useful for forming the solid phase of the detergent compositions herein comprises particles of a peroxygen bleaching agent. Such peroxygen bleaching agents may be organic or inorganic in nature. Inorganic peroxygen bleaching agents are frequently utilized in combination with a bleach activator.

Useful organic peroxygen bleaching agents include percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, Issued November 20, 1984; European Patent Application EP-A-133,354, Banks et al., Published February 20, 1985; and U.S. Patent 4,412,934, Chung et al., Issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid (NAPAA) as described in U.S. Patent 4,634,551, Issued January 6, 1987 to Burns et al.

Inorganic peroxygen bleaching agents may also be used in particulate form in the detergent compositions herein. Inorganic bleaching agents are in fact preferred. Such inorganic peroxygen compounds include alkali metal perborate and percarbonate materials, most preferably the percarbonates.

For example, sodium perborate (e.g. mono- or tetra-hydrate) can be used. Suitable inorganic bleaching agents can also include sodium or potassium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used. Frequently inorganic peroxygen bleaches will be coated with silicate, borate, sulfate or water-soluble surfactants. For example, coated percarbonate particles are available from various commercial sources such as FMC, Solvay Interox, Tokai Denka and Degussa.

Inorganic peroxygen bleaching agents, e.g., the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during use of the compositions herein for fabric laundering/bleaching) of the peroxy acid corresponding to the bleach activator. Various non-limiting examples of activators are disclosed in U.S. Patent 4,915,854, Issued April 10, 1990 to Mao et al.; and U.S. Patent 4,412,934 Issued November 1, 1983 to Chung et al. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical. Mixtures thereof can also be used. See also the hereinbefore referenced U.S. 4,634,551 for other typical bleaches and activators useful herein.

Other useful amido-derived bleach activators are those of the formulae:

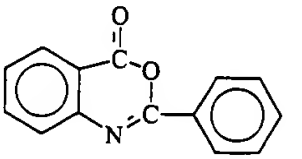
$$R^1N(R^5)C(O)R^2C(O)L \quad \text{or} \quad R^1C(O)N(R^5)R^2C(O)L$$

wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenol sulfonate.

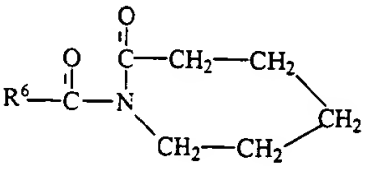
Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl) oxyben-zenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate and

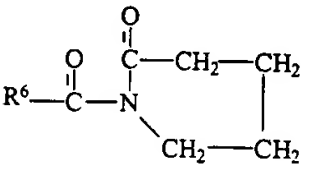
mixtures thereof as described in the hereinbefore referenced U.S. Patent 4,634,551. Such mixtures are characterized herein as (6-C_8-C_{10} alkamido-caproyl)oxybenzenesulfonate.

Another class of useful bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al. in U.S. Patent 4,966, 723, Issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of useful bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:





wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, Issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

If peroxygen bleaching agents are used as all or part of the essentially present particulate material, they will generally comprise from about 1% to 30% by weight of the composition. More preferably, peroxygen bleaching

agent will comprise from about 1% to 20% by weight of the composition. Most preferably, peroxygen bleaching agent will be present to the extent of from about 3% to 15% by weight of the composition. If utilized, bleach activators can comprise from about 0.5% to 20%, more preferably from about 1% to 10%, by weight of the composition. Frequently, activators are employed such that the molar ratio of bleaching agent to activator ranges from about 1:1 to 10:1, more preferably from about 1.5:1 to 5:1.

In addition, it has been found that bleach activators, when agglomerated with certain acids such as citric acid, are more chemically stable.

Surfactants

A type of particulate material which can be suspended in the non-aqueous liquid detergent compositions herein includes ancillary anionic surfactants which are fully or partially insoluble in the non-aqueous liquid phase. The most common type of anionic surfactant with such solubility properties comprises primary or secondary alkyl sulfate anionic surfactants. Such surfactants are those produced by the sulfation of higher C_8-C_{20} fatty alcohols.

Conventional primary alkyl sulfate surfactants have the general formula

$$ROSO_3^-M^+$$

wherein R is typically a linear C_8 - C_{20} hydrocarbyl group, which may be straight chain or branched chain, and M is a water-solubilizing cation. Preferably R is a C_{10} - C_{14} alkyl, and M is alkali metal. Most preferably R is about C_{12} and M is sodium.

Conventional secondary alkyl sulfates may also be utilized as the essential anionic surfactant component of the solid phase of the compositions herein. Conventional secondary alkyl sulfate surfactants are those materials which have the sulfate moiety distributed randomly along the hydrocarbyl "backbone" of the molecule. Such materials may be depicted by the structure

$$CH_3(CH_2)_n(CHOSO_3^-M^+)\,(CH_2)_mCH_3$$

wherein m and n are integers of 2 or greater and the sum of m + n is typically about 9 to 15, and M is a water-soiubilizing cation.

If utilized as all or part of the requisite particulate material, ancillary anionic surfactants such as alkyl sulfates will generally comprise from about 1% to 10% by weight of the composition, more preferably from about 1% to 5% by weight of the composition. Alkyl sulfate used as all or part of the particulate material is prepared and added to the compositions herein separately from the unalkoxylated alkyl sulfate material which may form part of the alkyl ether sulfate surfactant component essentially utilized as part of the liquid phase herein.

Organic Builder Material

Another possible type of particulate material which can be suspended in the non-aqueous liquid detergent compositions herein comprises an organic detergent builder material which serves to counteract the effects of calcium, or other ion, water hardness encountered during laundering/bleaching use of the compositions herein. Examples of such materials include the alkali metal, citrates, succinates, malonates, fatty acids, carboxymethyl succinates, carboxylates, polycarboxylates and polyacetyl carboxylates. Specific examples include sodium, potassium and lithium salts of oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids and citric acid. Other examples of organic phosphonate type sequestering agents such as those which have been sold by Monsanto under the Dequest tradename and alkanehydroxy phosphonates. Citrate salts are highly preferred.

Other suitable organic builders include the higher molecular weight polymers and copolymers known to have builder properties. For example, such materials include appropriate polyacrylic acid, polymaleic acid, and polyacrylic/polymaleic acid copolymers and their salts, such as those sold by BASF under the Sokalan trademark.

Another suitable type of organic builder comprises the water-soluble salts of higher fatty acids, i.e., "soaps". These include alkali metal soaps such as the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

If utilized as all or part of the requisite particulate material, insoluble organic detergent builders can generally comprise from about 1% to 20% by weight of the compositions herein. More preferably, such builder material can comprise from about 4% to 10% by weight of the composition.

Inorganic Alkalinity Sources

Another possible type of particulate material which can be suspended in the non-aqueous liquid detergent compositions herein can comprise a material which serves to render aqueous washing solutions formed from such compositions generally alkaline in nature. Such materials may or may not also act as detergent builders, i.e., as materials which counteract the adverse effect of water hardness on detergency performance.

Examples of suitable alkalinity sources include water-soluble alkali metal carbonates, bicarbonates, borates, silicates and metasilicates. Although not preferred for ecological reasons, water-soluble phosphate salts may also be utilized as alkalinity sources. These include alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Of all of these alkalinity sources, alkali metal carbonates such as sodium carbonate are the most preferred.

The alkalinity source, if in the form of a hydratable salt, may also serve as a desiccant in the non-aqueous liquid detergent compositions herein. The presence of an alkalinity source which is also a desiccant may provide benefits in terms of chemically stabilizing those composition components

such as the peroxygen bleaching agent which may be susceptible to deactivation by water.

If utilized as all or part of the particulate material component, the alkalinity source will generally comprise from about 1% to 15% by weight of the compositions herein. More preferably, the alkalinity source can comprise from about 2% to 10% by weight of the composition. Such materials, while water-soluble, will generally be insoluble in the non-aqueous detergent compositions herein. Thus such materials will generally be dispersed in the non-aqueous liquid phase in the form of discrete particles.

OPTIONAL COMPOSITION COMPONENTS

In addition to the composition liquid and solid phase components as hereinbefore described, the detergent compositions herein can, and preferably will, contain various optional components. Such optional components may be in either liquid or solid form. The optional components may either dissolve in the liquid phase or may be dispersed within the liquid phase in the form of fine particles or droplets. Some of the materials which may optionally be utilized in the compositions herein are described in greater detail as follows:

Optional organic additives

The detergent compositions may contain an organic additive. A preferred organic additive is hydrogenated castor oil and its derivatives.

Hydrogenated castor oil is a commercially available commodity being sold, for example, in various grades under the trademark CASTORWAX.RTM. by NL Industries, Inc., Highstown, New Jersey.Other Suitable hydrogenated castor oil derivatives are Thixcin R, Thixcin E, Thixatrol ST, Perchem R and Perchem ST. Especially preferred hydrogenated castor oil is Thixatrol ST.

The castor oil can be added as a mixture with ,for example stereamide.

The organic additive will be partially dissolved in the non-aqueous liquid diluent. To form the structured liquid phase required for suitable phase stabiiity and acceptable rheology, the organic additive is generally present to the extent of from about 0.05% to 20% by weight of the liquid phase. More preferably, the organic additive will comprise from about 0.1% to 10% by weight of the non-aqueous liquid phase of the compositions herein.

Optional Inorganic Detergent Builders

The detergent compositions herein may also optionally contain one or more types of inorganic detergent builders beyond those listed hereinbefore that also function as alkalinity sources. Such optional inorganic builders can include, for example, aluminosilicates such as zeolites. Aluminosilicate zeolites, and their use as detergent builders are more fully discussed in Corkill et al., U.S. Patent No. 4,605,509; Issued August 12, 1986, the disclosure of which is incorporated herein by reference. Also crystalline layered silicates, such as those discussed in this '509 U.S. patent, are also suitable for use in the detergent compositions herein. If utilized, optional inorganic detergent builders can comprise from about 2% to 15% by weight of the compositions herein.

Optional Thickening, Viscosity Control and/or Dispersing Agents

The detergent compositions herein may also optionally contain a polymeric material which serves to enhance the ability of the composition to maintain its solid particulate components in suspension. Such materials may thus act as thickeners, viscosity control agents and/or dispersing agents. Such materials are frequently polymeric polycarboxylates but can include other polymeric materials such as polyvinylpyrrolidone (PVP) and polymeric amine derivatives such as quaternized, ethoxylated hexamethylene diamines.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight of the polymer.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000, and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, Diehl, U.S. Patent 3,308,067, issued March 7, 1967. Such materials may also perform a builder function.

If utilized, the optional thickening, viscosity control and/or dispersing agents should be present in the compositions herein to the extent of from about 0.1% to 4% by weight. More preferably, such materials can comprise from about 0.5% to 2% by weight of the detergents compositions herein.

Optional Brighteners, Suds Suppressors and/or Perfumes

The detergent compositions herein may also optionally contain conventional brighteners, suds suppressors, silicone oils, bleach catalysts, and/or perfume materials. Such brighteners, suds suppressors, silicone oils, bleach catalysts, and perfumes must, of course, be compatible and non-reactive with the other composition components in a non-aqueous environment. If present, brighteners suds suppressors and/or perfumes will typically comprise from about 0.01% to 5% by weight of the compositions herein.

Suitable bleach catalysts include the manganese based complexes disclosed in US 5,246,621, US 5,244,594, US 5,114,606 and US 5,114,611. Especially preferred catalysts are the metallo-catalysts as described in co-pending US Patent applications Serial No. 60/040,629, Serial No. 60/039,915, Serial No. 60/040,222, Serial No. 60/040,156, Serial No. 60/040,115, Serial No. 60/038,714, Serial No. 60/039,920, filed on March 7, 1997.

COMPOSITION FORM

The particulate-containing liquid detergent compositions of this invention are substantially non-aqueous (or anhydrous) in character. While very small amounts of water may be incorporated into such compositions as an impurity in the essential or optional components, the amount of water should in no event exceed about 5% by weight of the compositions herein. More preferably, water content of the non-aqueous detergent compositions herein will comprise less than about 1% by weight.

The particulate-containing non-aqueous detergent compositions herein will be in the form of a liquid.

COMPOSITION PREPARATION AND USE

The non-aqueous liquid detergent compositions herein can be prepared by mixing non-aqueous liquid phase and by thereafter adding to this phase the additional particulate components in any convenient order and by mixing, e.g., agitating, the resulting component combination to form the stable compositions herein. In a typical process for preparing such compositions, essential and certain preferred optional components will be combined in a particular order and under certain conditions.

In a first step of a preferred preparation process, the anionic surfactant-containing liquid phase is prepared. This preparation step involves the formation of an aqueous slurry containing from about 30 to 60% of one or more alkali metal salts of linear C10-16 alkyl benzene sulfonic acid and from

about 2-15% of one or more diluent non-surfactant salts. In a subsequent step, this slurry is dried to the extent necessary to form a solid material containing less than about 4% by weight of residual water.

After preparation of this solid anionic surfactant-containing material, this material can be combined with one or more of the non-aqueous organic diluents to form the surfactant-containing liquid phase of the detergent compositions herein. This is done by reducing the anionic surfactant-containing material formed in the previously described pre-preparation step to powdered form and by combining such powdered material with an agitated liquid medium comprising one or more of the non-aqueous organic diluents, either surfactant or non-surfactant or both as herein before described. This combination is carried out under agitation conditions which are sufficient to form a thoroughly mixed dispersion of particles of the insoluble fraction of the co-dried LAS/salt material throughout a non-aqueous organic liquid diluent.

In a subsequent processing step, particulate material to be used in the detergent compositions herein can be added. Such components which can be added under high shear agitation include any optional surfactant particles, particles of substantially all of an organic builder, e.g. citrate and/or fatty acid and/or alkalinity source, e.g. sodium carbonate, can be added while continuing to maintain this admixture of composition components under shear agitation. Agitation of the mixture is continued, and if necessary, can be increased at this point to form a uniform dispersion of insoluble solid phase particulates within the liquid phase.

The non-aqueous liquid dispersion so prepared can be subjected to milling or high shear agitation. Milling conditions will generally include maintenance of a temperature between about 10 and 90°C, preferably between 20°C and 60°C. Suitable equipment for this purpose includes: stirred ball mills, co-ball mills (Fryma), colloid mills, high pressure homogenizers, high shear mixers, and the like. The colloid mill and high shear mixers are preferred for their high throughput and low capital and maintenance costs. The small particles produced in such equipment will generally range in size from 0.4- 150 microns.

Agitation is then continued, and if necessary, can be increased at this point to form a uniform dispersion of insoluble solid phase particles within the liquid phase.

In a second process step, the bleach precursor particles are mixed with the ground suspension from the first mixing step in a second mixing step. This mixture is then subjected to wet grinding so that the average particle size of the bleach precursor is less than 600 microns, preferably between 50 and 500 microns, most preferred between 100 and 400 microns.

After some or all of the foregoing solid materials have been added to this agitated mixture, the particles of the highly preferred peroxygen bleaching agent can be added to the composition, again while the mixture is maintained under shear agitation.

In a third processing step, the activation of the organic additive is obtained. The organic additives are subjected to wetting and dispersion forces to reach a dispersed state. It is well within the ability of a skilled person to activate the organic additive. The activation can be done according to that described by Rheox, in Rheology Handbook, A practical guide to rheological additives. There are basically three distinct stages. The first stage consists in adding the agglomerated powder in the solvent. This combination is carried out under agitation conditions (shear, heat, Stage 2) which are sufficient to lead to complete deagglomeration. With continued shear and heat development over a period of time, the solvent-swollen particles of the organic additive are reduced to their active state in stage 3.

In adding solid components to non-aqueous liquids in accordance with the foregoing procedure, it is advantageous to maintain the free, unbound moisture content of these solid materials below certain limits. Free moisture in such solid materials is frequently present at levels of 0.8% or greater (see method described below). By reducing free moisture content, e.g. by fluid bed drying, of solid particulate materials to a free moisture level of 0.5% or lower prior to their incorporation into the detergent composition matrix, significantly stability advantages for the resulting composition can be realized.

Free and Total Water Determinations:

For the purpose of this patent application, and without wanting to be bound by theory, we refer to "free water" as the amount of water that can be detected after removal of the solid, undissolved components of the product, whereas "total water" is referred to as the amount of water that is present in the product as a whole, be it bound to solids (e.g. water of hydration), dissolved in the liquid phase, or in any other form. A preferred method of water determinations is the so-called "Karl Fischer titration". Other methods than Karl Fischer titration, e. g. NMR, microwave, or IR spectroscopy, may also be suited for the determination of water in the liquid part of the product and in the full product as described below.

The "free water" of a formulation is determined in the following way. At least one day after preparation of the formula (to allow for equilibration), a sample is centrifuged until a visually clear layer, free of solid components, is obtained. This clear layer is separated from the solids, and a weighed sample is directly introduced into a coulometric Karl Fischer titration vessel. The water level determined in this way (mg water / kg clear layer) is referred to as "free water" (in ppm).

The "total water" is determined by first extracting a weighed amount of finished product with an anhydrous, polar extraction liquid. The extraction liquid is selected in such a way that interferences from dissolved solids are minimized. In most cases, dry methanol is a preferred extraction liquid. Usually, the extraction process reaches an equilibrium within a few hours - this needs to be validated for different formulations - and can be accelerated by sonification (ultrasonic bath). After that time, a sample of the extract is centrifuged or filtered to remove the solids, and a known aliqot then introduced into the (coulometric or volumetric) Karl Fischer titration cell. The value found in this way (mg water / kg product) is referred to as "total water" of the formulation.

Preferably, the non-aqueous liquid detergent compositions of the present invention comprise less than 5%, preferably less than 3%, most preferred less than 1% of free water.

Viscosity and yield measurements:

The particulate-containing non-aqueous liquid detergent compositions herein will be relatively viscous and phase stable under conditions of commercial marketing and use of such compositions. Frequently, the viscosity of the compositions herein will range from about 300 to 10,000 cps, more preferably from about 500 to 3000 cps. The physical stability of such formulations can also be determined by yield measurements. Frequently, the yield of the compositions herein will range from about 1 to 20 Pa, more preferably from about 1.5 to 10 Pa. For the purpose of this invention, viscosity and yield are measured with a Carri-Med CSL^2100 rheometer according to the method described herein below.

Rheological properties were determined by means of a constant stress rheometer (Carri-Med CSL^2100) at 25°C. A parallel-plate configuration with a disk radius of 40 mm and a layer thickness of 2 mm was used. The shear stress was varied between 0.1 Pa and 125 Pa. The reported viscosity was the value measured at a shear rate of about 20 s^{-1}. Yield stress was defined as the stress above which motion of the disk was detected. This implies that the shear rate was below 3×10^{-4} s^{-1}.

The compositions of this invention, prepared as herein before described, can be used to form aqueous washing solutions for use in the laundering and bleaching of fabrics. Generally, an effective amount of such compositions is added to water, preferably in a conventional fabric laundering automatic washing machine, to form such aqueous laundering/bleaching solutions. The aqueous washing/bleaching solution so formed is then contacted, preferably under agitation, with the fabrics to be laundered and bleached therewith.

An effective amount of the liquid detergent compositions herein added to water to form aqueous laundering/bleaching solutions can comprise

amounts sufficient to form from about 500 to 8,000 ppm of composition in aqueous solution. More preferably, from about 800 to 5,000 ppm of the detergent compositions herein will be provided in aqueous washing/bleaching solution.

The following examples illustrate the preparation and performance advantages of non-aqueous liquid detergent compositions of the instant invention. Such examples, however, are not necessarily meant to limit or otherwise define the scope of the invention herein.

EXAMPLE I

Preparation of Non-Aqueous Liquid Detergent Composition

1) Part of the Butoxy-propoxy-propanol (BPP) and a $C_{11}EO(5)$ ethoxylated alcohol nonionic surfactant (Genapol 24/50) are mixed for a short time (1-5 minutes) using a blade impeller in a mix tank into a single phase.

2) LAS is added to the BPP/NI mixture after heating the BPP/NI mixture up to 45°C.

3) If needed, liquid base (LAS/BPP/NI) is pumped out into drums. Molecular sieves (type 3A, 4-8 mesh) are added to each drum at 10% of the net weight of the liquid base. The molecular sieves are mixed into the liquid base using both single blade turbine mixers and drum rolling techniques. The mixing is done under nitrogen blanket to prevent moisture pickup from the air. Total mix time is 2 hours, after which 0.1-0.4% of the moisture in the liquid base is removed. Molecular sieves are removed by passing the liquid base through a 20-30 mesh screen. Liquid base is returned to the mix tank.

4) Additional solid ingredients are prepared for addition to the composition. Such solid ingredients include the following:

Sodium carbonate (particle size 100 microns)
Sodium citrate dihydrate
Maleic-acrylic copolymer (BASF Sokolan)
Brightener (Tinopal PLC)
Tetra sodium salt of hydroxyethylidene diphosphonic acid (HEDP)
Sodium diethylene triamine penta methylene phosphonate
Ethylenediamine disuccinic acid (EDDS)

These solid materials, which are all millable, are added to the mix tank and mixed with the liquid base until smooth. This takes approximately 1 hour after addition of the last powder. The tank is blanketed with nitrogen after addition of the powders. No particular order of addition for these powders is critical.

5) The batch is pumped once through a Fryma colloid mill, which is a simple rotor-stator configuration in which a high-speed rotor spins inside a stator which creates a zone of high shear. This reduces particle size of all of the solids. This leads to an increase in yield value (i.e. structure). The batch is then recharged to the mix tank after cooling.

6) The bleach precursor particles are mixed with the ground suspension from the first mixing step in a second mixing step. This mixture is then subjected to wet grinding so that the average particle size of the bleach precursor is less than 600 microns, preferably between 50 and 500 microns, most preferred between 100 and 400 microns.

7) Other solid materials could be added after the first processing step. These include the following :

Sodium percarbonate (400-600 microns)
Protease, cellulase and amylase enzyme prills (400-800 microns, specific density below 1.7 g/mL)
Titanium dioxide particles (5 microns)
Catalyst

These non-millable solid materials are then added to the mix tank followed by liquid ingredients (perfume and silicone-based suds suppressor fatty acid/silicone). The batch is then mixed for one hour (under nitrogen blanket).

The resulting composition has the formula set forth in Table I.

The catalyst is prepared by adding an octenylsuccinate modified starch, to water in the approximate ratio of 1:2. Then, the catalyst is added to the solution and mixed to dissolve. The composition of the solution is :

catalyst	5%
starch	32% (the starch includes 4-6% bound water)
water	63%

The solution is then spray dried using a lab scale Niro Atomizer spray drier. The inlet of the spray drier is set at 200°C, and the atomizing air is approximately 4 bar. The process air pressure drop is roughly 30-35 mm water. The solution feed rate is set to get an outlet temperature of 100°C. The powdered material is collected at the base of the spray drier.

The composition is :

catalyst	15%
starch (and bound water)	85%

The particle size is 15 to 100 um exiting the dryer.

TABLE I

Non-Aqueous Liquid Detergent Composition with Bleach

Component	Wt % Active	Wt % Active
LAS Na Salt	16	15
C11E0=5 alcohol ethoxylate	21	20
BPP	19	19
Sodium citrate	4	5

[4-[N-nonanoyl-6-aminohexanoyloxy] benzene sulfonate] Na salt	6	7
Chloride salt of methyl quarternized polyethoxylated hexamethylene diamine	1.2	1
Ethylenediamine disuccinic acid	1	1
Sodium Carbonate	7	7
Maleic-acrylic copolymer	3	3
Protease Prills	0.40	0.4
Amylase Prills	0.8	0.8
Cellulase Prills	0.50	0.5
Sodium Percarbonate	16	-
Sodium Perborate	-	15
Suds Suppressor	1.5	1.5
Perfume	0.5	0.5
Titanium Dioxide	0.5	0.5
Brightener	0.14	0.2
Thixatrol ST	0.1	0.1
Catalyst	0.03	0.03
Speckles	0.4	0.4
Miscellaneous up to 100%		

The resulting Table I composition is a structured, stable, pourable anhydrous heavy-duty liquid laundry detergent which provides excellent enzymatic stain and soil removal performance when used in normal fabric laundering operations. The viscosity measurement at 25°C is about 2200 cps at shear rate 20 s^{-1}, yield is about 8.9 Pa at 25°C.

WHAT IS CLAIMED IS:

1. A non-aqueous liquid detergent composition comprising a bleaching agent and/or bleach precursor, one or more of an enzyme particle, characterized in that said detergent composition further comprises ethylenediamine-N, N'-disuccinic acid, or alkali metal, alkaline earth, ammonium or substituted ammonium salts thereof, or mixtures thereof.

2. A non-aqueous detergent composition according to claim 1 wherein said enzyme is selected from cellulases, proteases, amylases, lipases and/or peroxidases.

3. A non-aqueous detergent composition according to claim 2 wherein said enzyme is selected from amylases.

4. A non-aqueous detergent composition according to claims 1-3 wherein said bleaching agent is selected from percarbonate and/or perborate.

5. A non-aqueous detergent composition according to claim 4, wherein said bleach precursor is selected from (6-octanamido-caproyl) oxybenzenesulfonate, (6-nonanamidocaproyl)oxy benzene sulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof.

6. A non-aqueous liquid detergent composition according to claims 1-5 comprising less than 5% of free water.

INTERNATIONAL SEARCH REPORT

Internatior Application No
PCT/US 98/13187

A. CLASSIFICATION OF SUBJECT MATTER

C 11 D 17/00,C 11 D 3/386,C 11 D 3/33,C 11 D 3/39

According to International Patent Classification (IPC) or to both national classification and IPC6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 11 D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0598693 A1 (THE PROCTER & GAMBLE) 25 May 1994 (25.05.94), page 3, lines 40-52, claims. --	1-6
A	GB 2288607 (THE PROCTER & GAMBLE) 25 October 1995 (25.10.95), examples, claim 1. --	1-2
A	US 4704233 A (HARTMAN et al.) 03 November 1987 (03.11.87), column 9, lines 1-24, examples, claims. --	1
A	EP 0565017 A2 (SOLVAY INTEROX) 13 October 1993 (13.10.93),	1,4

[X] Further documents are listed in the continuation of box C.

[ ] Patent family members are listed in annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 September 1998	27. 10. 98

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	SEIRAFI e.h.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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	the whole document (cited in the application). ----	